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# AUTOMATION OF PREPARATION OF NONMETALLIC SAMPLES FOR ANALYSIS BY ATOMIC ABSORPTION AND INDUCTIVELY COUPLED PLASMA SPECTROMETRY

A. Wittmann and G. Willay

Translation of "Automatisation de la préparation des échantillons non métalliques pour l'analyse par absorption atomique et par torche à plasma", Cahiers d'Informations Techniques/Revue de Metallurgie, Vol. 82, No. 5, 1985, pp. 399-410.

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16. Abstract For a rapid preparation of solutions intended for analysis by inductively coupled plasma emission spectrometry or atomic absorption spectrometry, an automatic device called Plasmasol was developed. This apparatus used the property of nonwettability of glassy C to fuse the sample in an appropriate flux. The sample-flux mixture is placed in a composite crucible, then heated at high temperature, swirled until full dissolution is achieved, and then poured into a water-filled beaker. After acid addition, dissolution of the melt, and filling to the mark, the solution is ready for analysis. The analytical results obtained, either for oxide samples or for prereduced iron ores show that the solutions prepared with this device are undistinguishable from those obtained by manual dissolutions done by acid digestion or by high temperature fusion. Preparation reproducibility and analytical tests illustrate the performance of Plasmasol.

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# AUTOMATION OF PREPARATION OF NONMETALLIC SAMPLES FOR ANALYSIS BY ATOMIC ABSORPTION AND INDUCTIVELY COUPLED PLASMA SPECTROMETRY[1]

A. Wittmann and G. Willay
IRSID

## Introduction

The optical emission spectrometry with inductively coupled plasma (SEO-ICP) as an excitation source is a method for analysis which is spreading to more and more laboratories. /399*

In these days, all the large ironworks laboratories are equipped with them and there is reason to believe that this tendency is going to become a general practice by the end of the 1980's. With this spectrometric technique, the measurement time is very low, practically negligible in comparison to the time necessary in order to prepare the solution to be analyzed. Faced with the non-existence of mechanized means for placing into solution the non-metallic samples of the ironworks, the IRSID has decided to construct an apparatus capable of carrying out such a task in a relatively short time and presenting a minimum of harmful effects for the environment. Derived from its CECA no. 6210-GA/3/307 investigation, the PERL'X, of which more than 100 examples are in service at the present time, has been taken as the base model for the construction of the new apparatus. This apparatus is called PLASMASOL. The preparations are accomplished by fusion-dilution in a special crucible called "composite cricible". The operational mode has been applied to the majority of non-metallic products encountered in ironworks, as well as to the pre-reduced iron

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[1] Text of the IRSID RE 1112 report. CECA no. 7210 GD/301 investigation. The authors express their gratitude to Michel Villiere and Francis Kop for their collaboration in the analytical realm, as well as to Gilbert Kilhofer of the Soled for his technical assistance in the construction of the Plasmasol prototype.

* Numbers in the margin indicate pagination of the foreign text.

minerals.

Apparatus and Technique /400

The method of preparation consists of a fusion-dilution at high temperature in an appropriate flux, followed by the dissolution of the product in dilute acid. After cooling, transfer into a volumetric flask and return to volume with water , the solution is ready for the analysis.

The "Plasmasol"

The apparatus constructed by the IRSID is called Plasmasol (IRSID patent AFBI 667) [1]; represented in figure 1, it allows transformation of a sample in the form of a powder into a liquid solution. The sample-flux mixture is placed into a "composite crucible" then placed into a mobile furnace which rotates around a horizontal axis. When the fusion-dilution is terminated, the furnace rotates by 120° and the mixture in fusion is poured into a 200 ml teflon beaker containing 50 ml of deionized water and placed on a magnetic stirrer (figure 2). The heating is ensured by a high frequency furnace. This method is characterized by its effectiveness, its low noise level and by the low consumption of energy. The crucible is placed in the induction coil of the furnace, at the interior of a fireproof cylinder in order to avoid any contact with the inductor. The furnace is attached on a vertical disk movable within its plane around an akle passing through its center. The furation of the stirring, the amplitude of the oscillations and the strength of the heating can be programmed and controlled with the assistance of a microprocessor.

The pouring of the product from the fusion has occurred after the last oscillation of the furnace. The product is poured into the beaker containing the water and a small magnetic rod and it is placed into a housing above the magnetic stirrer. Shortly before the pouring, this stirrer imparts a movement of rotation to the water. The

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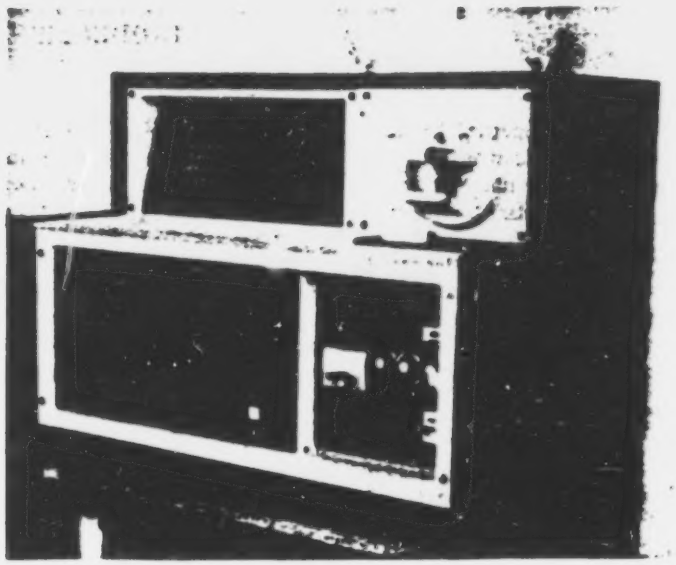

Figure 1. The Plasmasol apparatus.

Figure 2. The pouring of the mixture.

sudden contact of the incandescent liquid with the water induces the /401
disintegration of the glass into fine particles. The remainder of
the preparation is carried out manually. The beaker is placed on a

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hot plate and 10 ml of dilute hydrochloric acid (1 + 1) are added. Three to five minutes later, when the dissolution is finished, the solution is poured into a volumetric flask, brought to volume, possibly filtered if it turns out to be necessary, then measured.

The "Composite Crucible"

The "Composite Crucible" (IRSID patent AFBI 661) [2] is constituted of two containers placed one inside the other with a very small interval between them. The exterior container is a platinum alloy, that at the interior is of vitreous carbon. This last has a wall thickness of 1 or 2 mm and it is placed in such a fashion within the platinum crucible that it overlaps by 1 to 2 mm the upper edge of the platinum crucible (figure 3). In this fashion, the combustion of the carbon crucible during the fusion is limited to this upper portion. Experience has demonstrated that more than thirty fusions could be carried out with the same vitreous carbon crucible by progressively reinforcing this with the assistance of ceramic blocks (figure 4). The action of the high frequency is concentrated on the exterior crucible of platinum alloy which rapidly equilibrates its temperature through radiation, which leads to a uniform temperature at the interior of the vitreous carbon crucible.

Figure 3. The composite crucible.

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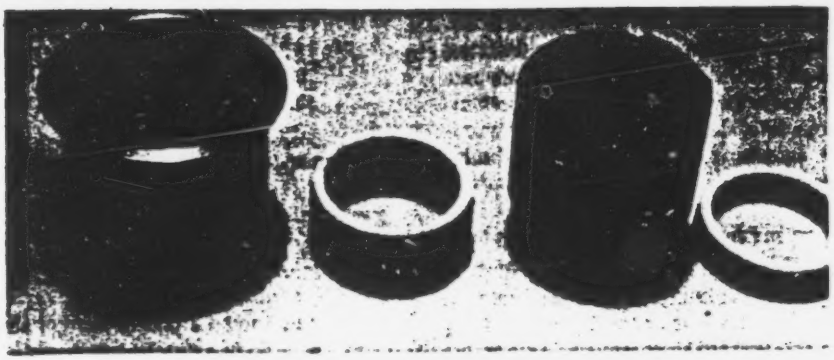

Figure 4. Reinforcing ceramic blocks.

The vitreous carbon crucible presents two major advantages: first, certain fluxes such as lithius metaborate, lithium tetraborate or mixtures formed of one part of boric acid and five parts of lithium metaborate do not adhere to the walls, nor to the base of the crucible after the fusion and the pouring. The recovery of the fusion product is quantitative. Thus, no intermediate weight is necessary at the time of the preparation of the samples. In other respects, since it is possible to avoid the cleaning stage, the crucible is immediately ready for the next fusion. The second advantage of the vitreous carbon crucible with respect to the platinum alloy crucible resides in the fact that it can be employed in order to prepare samples containing metallic particles such as the pre-reduced iron minerals, the steelworks dust or the secondhand fireclay, which present risks of deterioration of the platinum. /402

Selection of the Fluxes

The selection of the flux is based on three criteria: its capability to dissolve the sample, its non-adherence to the vitreous carbon crucible and its purity in elements to be titrated.

The most frequently cited fluxes in the literature are the tetraborates of sodium, lithium and strontium, lithium metaborate, lithium metaphosphate, boric anhydride, sodium peroxide, the carbonates of sodium, lithium and ammonium, the fluorides of sodium and lithium or

mixtures of these various fluxes. Each of these fluxes has a particular range of application; the same is true for certain mixtures. More particularly concerning the ironworks products, there are primarily the fluxes with a base of lithium tetraborate and lithium metaborate which are the most effective. The sodium tetraborate alone or added to other fluxes, as well as the lithium metaphosphate and sodium peroxide, are also employed for the placement into solution of certain types of products encountered in ironworks.

The behavior of these various fluxes vis-a-vis vitreous carbon is variable. With the operational mode for the preparation of the samples, it is imperative to recover the totality of the fusion product. Also, fluxes such as sodium tetraborate and sodium peroxide employed alone are to be proscribed. This is also true for the lithium carbonate-boric anhydride mixture. The behavior of the boric anhydride-lithium metaborate mixtuer is variable as a function of the ratio of the two constituents: thus, for an equal portion of each constituent, the recovery after fusion is very incomplete, hwile with one part of boric anhydride and five parts of lithium metaborate, the recovery is total.

Among the various mixtures tested in the course of the tests of fluxes, two in particular have given satisfaction:

-the boric anhydride-lithium metaborate mixture 15-85;

-the Fluosid 21 flux (marketed by Industrie Chimique of the High Countries, Micheville, F 54190 Villerupt).

This last flux contains 75.5% of lithium tetraborate, 3.5% of boric anhydride and 21% of lanthanium oxide. It is presently used to make beads for X-ray fluorescence and it is very effective for the placement into solution of practically all the samples, except those having chromium contents greater than 25%. In other respects, this flux is pre-molten and granulated (granulometry comprised between 500 and 100 µm), which facilitates the dissolution of the samples containing significant contents of carbonates while avoiding the creep of the sample-flux mixture at the time of the beginning of the heat-

ing.

However, it is necessary to remark, concerning the fluxes utilizable in order to make the preparations with the "Plasmasol", that the behavior of the flux-sample mixture also depends on the nature of the sample and that there is then reason to determine if there are particles of matter which adhere to the crucible.

Spectrometers and Inductively Coupled Plasma

While still being capable of being analyzed by other chemical or physicochemical techniques, the solutions prepared with the Plasmasol have all been measured by ICP-SEO. Two spectrometer-inductively coupled plasma assemblages have been implemented.

Sequential Assemblage

The sequential assemblage includes:

-an ARL Quantoscan 35000 monochromator under vacuum having the following characteristics:

Czerny Turner mounting
Focal length of mirrors: 1 m
2160 lines/mm plane network
dispersion: 0.4 nm/mm, approximately
spectral range: 175 to 460 nm,
inlet slit: 20 µm
outlet slit: 20 µm
photomultipliers: 1 for reference
1 for measurement
Thermal regulation by circulation of oil at constant temperature

-a DURR inductively coupled plasma including:

a generator with an output of 5 kVA, a frequency of 50 MHz, with tuned lines fo = $\frac{C}{4l}$, with fo: central frequency
C: speed of light
l: length of the lines

-a detachable inductively coupled plasma with 2 pipes

-an inductor with 5 whorls
-an ultrasonic nebulizer.

Multichannel Assemblage /403

The multichannel assemblage is composed in the following fashion:

-a Jobin-Yvon JY 48 VEP spectrometer having as characteristics:
Paschen-Runge mounting, 1 m diameter
holographic network engraved with 2550 lines/mm
spectral range: 130 to 450 nm
dispersion: 0.39 nm/mm in the first order
assemblage under vacuum
spark stand at 90°
plasma stand in line
spectral lines (in nm):

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fe: | 271.4 | Si: | 288.1 | Ca: | 393.3 | Al: | 396.1 | Ti: | 337.2 |
| Mg: | 337.2 | P: | 178.3 | Mn: | 293.30 | Pb: | 220.3 | Cr: | 267.7 |

-a DURR inductively coupled plasma including: a generator with an output of 2.2 kVA, a frequency of 56 MHz, with tuned lines
-a detachable Jobin-Yvon inductively coupled plasma with argon sheathing according to INSA
-an indicator with 6 whorls
-an argon humidifier
-a GMK nebulizer
-a peristaltic pump with 8 rollers.

Operational Modes and Analytical Results. Case of Oxide Products

There are primarily two families of products which have been studied in view of their placement into solution by the Plasmasol. It is a question of oxides, objects of this chapter, and pre-reduced iron minerals, objects of the following chapter.

The oxide products include the iron minerals, the agglomerates of iron minerals, the hot furnace slags, the steelworks slags, the

dusts, the fireclays, in sum all the non-metallic samples capable of being encountered in the ironworks. The diagram for the preparation is indicated in figure 5. In order to accelerate the fusion processes, the temperature is brought to 1250°C during the first part of the preparation. Then, when all is molten, the temperature for homogenization and pouring is brought to 1080-1100°C.

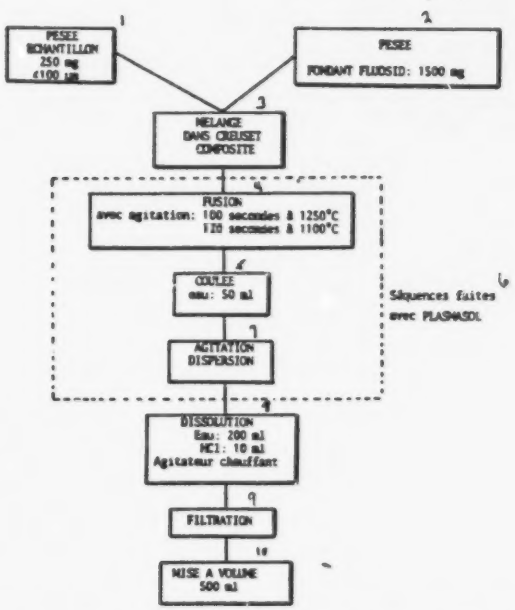


Figure 5. Diagram of the preparation for the titration of iron.

Key: 1-Sample weight 2-Fluosid flux weight 3-Mixture in composite crucible 4-Fusion with stirring: 100 seconds at 1250°C, 120 seconds at 1100°C 5-Pouring, water: 50 ml 6-Sequences made with Plasmasol 7-Stirring, dispersion 8-Dissolution, water: 200 ml, HCl: 10 ml, heating stirrer 9-Filtration 10-Return to volume, 500 ml

Proceeding in this fashion allows in addition reduction of the risk of sticking of the fusion product on the vitreous carbon crucible. After the fusion, the redissolution of the fusion residue already divided is made with heat in a concentrated hydrochloric acid-5% deionized water mixture. The final dilution is 0.5 g of sample per liter of solution. If a filtration turns out to be necessary, it

is carried out after the return to volume.

Titration of the Iron by Volumetry

A first series of tests, with the goal of verifying the validity of the placement into solution carried out with the Plasmasol, concerned the titration of the iron by volumetry. The titration was carried out in sulfo-phosphoric medium and in the presence of diphenylamine sodium sulfonate with the assistance of a standardized solution of potassium bichromate. Previously, the iron had been reduced by stannous chloride, whose excess was destroyed by mercuric chloride.

Two samples of different origin and composition have been tested. It is a question of the products:

612-1, MRC of Lorraine mineral agglomerates, whose placement into solution by acid route is easily accomplished;

606-1, MRC of rich minerals of the Ouenza type which is normally difficult to place into solution by acid route alone.

These two samples have the composition indicated in table 1. /404

TABLE 1. COMPOSITION (IN %) OF SAMPLES 612-1 AND 606-1.

| Samp. | Fe | Si | Ca | Al | Ti | Mg | P | Mn |
|---|---|---|---|---|---|---|---|---|
| 612-1 | 42,43 | 5,94 | 12,06 | 3,00 | 0,151 | 1,20 | 0,885 | 0,363 |
| 606-1 | 59,66 | 1,04 | 1,04 | 0,34 | 0,019 | 0,32 | 0,026 | 2,59 |

Two preparations have been carried out and the solutions obtained have been titrated for iron (table 2).

These very good results, obtained with a universally kncwn and applied method of titration, demonstrate the excellent reproducibil-

TABLE 2. RESULTS OF ANALYSES OF IRON (IN %) OF SAMPLES 612-1 & 606-1

| Certificate | | | Analysis | | | | |
|---|---|---|---|---|---|---|---|
| Samp. | Fe | | Fe % volumetry | Fe % extreme values | $s_R$ | $c_v$ % | N number |
| | $\bar{x}$ % | $s_M$ | | | | | |
| 612-1 | 42,43 | 0,13 | 42,30 | 42,20 - 42,40 | 0,09 | 0,21 | 12 |
| 606-1 | 59,66 | 0,14 | 59,77 | 59,50 - 60,00 | 0,16 | 0,27 | 12 |

$\bar{X}$ is the interlaboratory mean of the certification circuit
$s_M$ is the corresponding interlaboratory standard deviation
$s_R$ is the reproducibility of the preparation
$c_v$ is the coefficient of variation.

ity obtained with the technique for placement into solution described associated with the use of the Plasmasol.

Analysis by ICP-SEO

With the hope of also realizing good placements into solution for the other elements, this method of preparation has been employed in order to make solution designed to be analyzed by optical emission spectrometer with excitation by inductively coupled plasma. The advantage of the ICP-SEO and in particular the use of the JY 48 consists of being able to realize an appreciable gain of time with respect to the other techniques for analysis by wet route.

In order to test the preparation method, seven samples representative of the range of non-metallic products of the ironworks has been examined. Taking into account the variety of the matrices, the composition of the flux has been changed slightly by the addition of a nitrate with the goal of facilitating the placement into solution. Strontium nitrate has finally been preferred over lithium nitrate, the risk of adherence to the crucible being lower. The diagram of this new preparation is demonstrated in figure 6.

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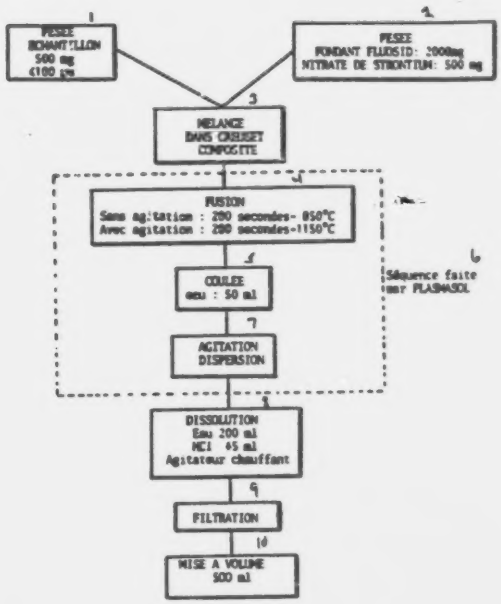


Figure 6. Diagram of the preparation of the oxide products. Key: 1-Sample weight 2-Weight Fluosid flux: 2000 mg, strontium nitrate: 500 mg 3-Mixture in composite cricible 4-Fusion, without stirring: 200 seconds-850°C, with stirring: 200 seconds-1150°C 5-Pouring, water: 50 ml 6-Sequence made by Plasmasol 7-Stirring, dispersion 8-Dissolution, water 200 ml, HCl 75 ml, Heating stirring 9-Filtration 10-Return to volume.

Table 3 gives the results obtained. There are precisely defined /405 the value certified by the MRC, as well as the interlaboratory standard deviation of the certificate, the reproducibility of the measurement obtained for 10 consecutive measurements, which is characterized by the standard deviation $s_r$, as well as the preparation reproducibility (including the measurement reproducibility) obtained on 10 preparations of the sample 611-1, which is characterized by the standard deviation $s_R$.

This table demonstrates that the preparation and measurement dispersions are finally very close to one another. This would say that the preparation by the Plasmasol does not degrade the analysis. Howver, it would be desirable that the measurement dispersion could

TABLE 3. REPRODUCIBILITY-SAMPLE 611-1.

| | Fe | Si | Ca | Al | Ti | Mg | P | Mn |
|---|---|---|---|---|---|---|---|---|
| % Content | 62,22 | 2,67 | 2,85 | 0,69 | 0,035 | 0,32 | 0,036 | 1,97 |
| $s_M$ | 0,16 | 0,04 | 0,10 | 0,03 | 0,003 | 0,04 | 0,008 | 0,06 |
| Parent solutions | | | | | | | | |
| Reproducibility measurement $s_r$ | 0,28 | 0,008 | 0,013 | 0,002 | 0,0002 | 0,0013 | 0,0032 | 0,008 |
| n = 10 (% content) | | | | | | | | |
| Coefficient of variation | 0,45 | 0,30 | 0,46 | 0,29 | 0,57 | 0,41 | 10,9 | 0,40 |
| Reproducibility preparation $s_R$ | 0,33 | 0,02 | 0,02 | 0,003 | 0,0006 | 0,0017 | 0,0027 | 0,015 |
| n = 10 (% content) | | | | | | | | |
| Coefficient of variation | 0,56 | 0,76 | 0,71 | 0,72 | 1,1 | 0,53 | 9,4 | 0,76 |
| Daughter solutions | | | | | | | | |
| Reproducibility measurement $s_r$ | 0,09 | 0,28 | 0,013 | 0,002 | 0,0006 | 0,0003 | 0,018 | 0,0054 |
| Coefficient of variation | 0,14 | 13,3 | 0,46 | 0,29 | 1,1 | 0,09 | 60 | 0,27 |
| Reproduciblity preparation $s_R$ | 0,26 | 0,50 | 0,009 | 0,007 | 0,0007 | 0,001 | 0,016 | 0,009 |
| n = 10 (% content) | | | | | | | | |
| Coefficient of variation | 0,41 | 20,1 | 0,31 | 1,0 | 2,0 | 0,3 | 55 | 0,46 |

be improved still more.

Similar tests of reproducibility have been carried out on Lorraine minerals, hot oven slags and fireclays. The results obtained are not indicated here, but they lead to the same conclusion.

## Analyses

Two routes exist in order to ensure the accuracy of an analysis: recourse to the MRC or to synthetic samples. While this last route is difficult for certain physical methods of analysis, it is possible on the contrary in the case of ICP-SEO. However, even at the level of synthetic standardization, there is still the choice between two methods. One consists of starting with standardization solutions, either pures or simulating the matrix; the other calls on the reconstitution of the standard sample by starting with oxides and pure salts. In the course of the various analytical tests carried out during the furaction of this contract, these various routes have been explored.

Standardization by MRC

The 7 MRC whose composition appears in table 4 have been prepared according to the method described above (figure 6), then measured and the data processed with the assistance of first and second degree regressions calculated from the intensities obtained and the certified contents. The 1000 mg/l solutions have been measured at constant time and the raw intensity has been taken into account, while the dilute 100 mg/l solutions, to which there has been added nickel as an internal standard, have been measured by ratio with respect to the nickel. The nickel content of the solutions was 500 mg/l. Table 5 demonstrates the results obtained. It is necessary to remark that for calcium, it is the second degree regression which leads to the result pointed out for the 1000 mg/l solutions, while for the dilute solutions, the intensity-content correlation is linear. It is possible to see in this table that the dilute solutions lead to an increase in the imprecision of the analysis for elements such as silicon, aluminum and phosphorous, while for iron, it is the inverse phenomena which is produced: a slight improvement of the dispersion is in fact observed. The standard deviation by comparison for iron between the values found by ICP-SEO and the reference values being established at s = 0.42%, it is to be noted that this value is high with respect to the performances of other methods of analysis by physical routes, such as for example the X-ray fluorescence.

Standardization by Synthetic Solutions

In order to be free of the reference samples and have access to analyses independent of any other method of titration, it is possible to practice synthetic standardization. The utilization of two solutions and their mixtures can allow, as table 6 demonstrates, the covering to the entire range of contents encountered for these seven samples. /407

The samples have been measured by ICP-SEO as previously, on a an absolute 1000 mg/l solution and on a 100 mg/l solution by ratio

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TABLE 4. COMPOSITION OF THE CERTIFIED REFERENCE MATERIALS (MRC) /406
(MEAN VALUE $\bar{X}$ AND STANDARD DEVIATION $S_M$ IN %).

| Element | | Iron Minerals 679.1 | Iron Minerals 679.2 | Hot Oven Slag 878.1 | Ironwork Slag 879.1 | Electric Furnace Dust 876.1 | Hot Oven Dust PHF.2* | Laterite 610.1 |
|---|---|---|---|---|---|---|---|---|
| Fe | $\bar{x}$ | 26.2 | 59.9 | 8.6 | 18.9 | 24.85 | 31.7 | 47.6 |
| | $S_M$ | 0.08 | 0.085 | 0.3 | 0.19 | 0.17 | 0.20 | 0.35 |
| Si | $\bar{x}$ | 3.6 | 4.2 | 15.7 | 4.12 | 1.71 | 5.46 | 3.16 |
| | $S_M$ | 0.04 | 0.02 | 0.08 | 0.03 | 0.04 | 0.08 | 0.04 |
| Ca | $\bar{x}$ | 18.0 | 0.65 | 25.6 | 31.2 | 3.63 | 13.6 | (8.1) |
| | $S_M$ | 0.14 | 0.015 | 0.13 | 0.26 | 0.13 | | |
| Al | $\bar{x}$ | 1.99 | 0.66 | 8.6 | 0.62 | 0.33 | 2.80 | 1.96 |
| | $S_M$ | 0.05 | 0.002 | 0.10 | 0.016 | 0.026 | | 0.10 |
| Ti | $\bar{x}$ | 0.106 | 0.045 | 0.37 | 0.32 | 0.017 | 0.12 | 0.015 |
| | $S_M$ | 0.005 | 0.003 | 0.01 | 0.005 | 0.004 | | 0.005 |
| Mg | $\bar{x}$ | 0.69 | 0.14 | 5.80 | 1.32 | 1.31 | 1.10 | 1.86 |
| | $S_M$ | 0.02 | 0.012 | 0.07 | 0.03 | 0.003 | | 0.11 |
| P | $\bar{x}$ | 0.55 | 0.018 | 0.013 | 3.69 | 0.178 | 0.8 | 0.007 |
| | $S_M$ | 0.009 | 0.002 | 0.001 | 0.003 | 0.007 | | 0.002 |
| Mn | $\bar{x}$ | 0.295 | 0.025 | 0.99 | 3.65 | 2.84 | 0.30 | 0.58 |
| | $S_M$ | 0.015 | 0.002 | 0.03 | 0.04 | 0.04 | | 0.016 |

*This sample was not certified

to the nickel as internal standard. The results obtained are indicated in table 7. Iron and calcium were run according to a second degree relationship. The dilute solutions reduce the precision for silicon, aluminum, magnesium and phosphorous. The precision obtained is very poor for iron and this is aggravated by a systematic deviation in disfavor of the standardization by synthetic solution. This deviation is situated between 0.7 and 0.8%. Its origin is probably connected to the difference of composition between the synthetic solutions and the actual solutions. A systematic deviation is also observed for calcium. It is lower and of opposite sign.

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TABLE 5. RESULTS OBTAINED WITH STANDARDIZATION BY MRC.

| | | 679-1 | 680-1 | 878-1 | 879-1 | 876-1 | PHF-2 | 618-1 | s |
|---|---|---|---|---|---|---|---|---|---|
| Fe | x̄ | 34,2 | 59,9 | 0,60 | 18,9 | 34,85 | 31,7 | 67,A | |
| | $s_{bl}$ | 0,00 | 0,885 | 0,3 | 0,19 | 0,17 | 0,20 | 0,35 | |
| | Solutions 1000 mg/l | 34,0 | 59,7 | 0,56 | 19,3 | 34,76 | 31,2 | 67,9 | 0,35 |
| | 100 mg/l | 34,2 | 60,0 | 0,53 | 19,2 | 34,78 | 31,5 | 67,A | 0,16 |
| Si | x̄ | 3,A | 4,2 | 15,7 | 4,12 | 1,71 | 5,A6 | 3,16 | |
| | $s_{bl}$ | 0,04 | 0,02 | 0,08 | 0,03 | 0,04 | 0,08 | 0,04 | |
| | Solutions 1000 mg/l | 3,67 | 4,23 | - | 4,15 | 1,63 | 5,36 | 3,19 | 0,07 |
| | 100 mg/l | 3,76 | 4,19 | | 4,12 | 1,89 | 5,38 | 2,70 | 0,27 |
| Ca | x̄ | 18,0 | 0,45 | 25,A | 31,2 | 3,63 | 13,A | 08,11 | |
| | $s_{bl}$ | 0,14 | 0,015 | 0,13 | 0,26 | 0,13 | | | |
| | Solutions 1000 mg/l | 18,1 | 0,51 | 25,A | 31,16 | 3,19 | 13,62 | 0,19 | 0,12 |
| | 100 mg/l | 18,2 | 0,A1 | 25,18 | 31,17 | 3,60 | 13,51 | 0,04 | 0,13 |
| Al | x̄ | 1,99 | 0,66 | 0,A0 | 0,A2 | 0,33 | 2,0 | 1,96 | |
| | $s_{bl}$ | 0,05 | 0,002 | 0,10 | 0,016 | 0,026 | | 0,10 | |
| | Solutions 1000 mg/l | 2,01 | 0,61 | [illegible] | 0,55 | 0,32 | 2,75 | 1,90 | 0,067 |
| | 100 mg/l | 2,05 | 0,59 | 0,A1 | 0,592 | 0,29 | 2,78 | 1,82 | 0,096 |
| Ti | x̄ | 0,106 | 0,045 | 0,37 | 0,32 | 0,047 | 0,12 | 0,015 | |
| | $s_{bl}$ | 0,005 | 0,003 | 0,01 | 0,005 | 0,006 | | 0,005 | |
| | Solutions 1000 mg/l | 0,106 | 0,040 | 0,35 | 0,32 | 0,044 | 0,149 | 0,005 | 0,015 |
| | 100 mg/l | 0,108 | 0,038 | 0,35 | 0,32 | 0,045 | 0,148 | 0,004 | 0,015 |
| Mg | x̄ | 0,69 | 0,14 | 5,8 | 1,32 | 1,31 | 1,1 | 1,86 | |
| | $s_{bl}$ | 0,02 | 0,012 | 0,07 | 0,03 | 0,003 | | 0,11 | |
| | Solutions 1000 mg/l | 0,67 | 0,146 | 5,79 | 1,33 | 1,31 | 1,01 | 1,91 | 0,044 |
| | 100 mg/l | 0,70 | 0,15 | 5,80 | 1,36 | 1,33 | 1,00 | 1,84 | 0,045 |
| P | x̄ | 0,55 | 0,018 | 0,013 | 3,69 | 0,128 | 0,8 | 0,007 | |
| | $s_{bl}$ | 0,009 | 0,002 | 0,001 | 0,003 | 0,007 | | 0,002 | |
| | Solutions 1000 mg/l | 0,552 | 0,002 | 0,008 | 3,69 | 0,104 | 0,784 | - | 0,013 |
| | 100 mg/l | 0,56 | 0,013 | * 0,119 | 3,69 | 0,097 | 0,76 | - | 0,014 |

* Pollution ?

TABLE 6. SYNTHETIC SOLUTIONS: RANGE OF CONTENTS (IN %).

| Fe | Si | Ca | Al | Ti | Mg | P |
|---|---|---|---|---|---|---|
| 0 à 60 | 0 à 20 | 0 à 40 | 0 à 10 | 0 à 1 | 0 à 10 | 0 à 5 |

Standardization by "Synthetic Samples"

With the goal of improving the precision of the results obtained by synthetic standardization, there has been recourse to samples standardized with pure and well defined elemental compounds. These "synthetic samples" have been prepared by Dr. Staats in the ironworks of Dilligen (RFA) and currently serve in this factory for standardi-

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TABLE 7. RESULTS OBTAINED WITH STANDARDIZATION BY SYNTHETIC SOLUTIONS.

| | | 679-1 | 680-1 | 678-1 | 879-1 | 876-1 | PMF-2 | 610-1 | s % | d % rel.-ICP |
|---|---|---|---|---|---|---|---|---|---|---|
| Fe | $\bar{x}$ | 24.2 | 19.9 | 0.60 | 18.9 | 24.85 | 31.7 | 47.6 | | |
| | solution 1000 mg/l | 23.6 | 18.9 | 0.70 | 18.6 | 24.9 | 32.7 | 45.0 | 1.16 | - 0.79 |
| | 100 mg/l | 23.8 | 18.9 | 1.0 | 18.8 | 24.6 | 31.6 | 44.7 | 1.25 | - 0.76 |
| Si | $\bar{x}$ | 3.60 | 4.2 | 15.7 | 4.12 | 1.71 | 3.46 | 3.16 | | |
| | solution 1000 mg/l | 3.66 | 4.20 | - | 4.36 | 1.86 | 3.37 | 3.17 | 0.13 | - 0.05 |
| | 100 r g/l | 3.61 | 4.00 | - | 4.27 | 1.80 | 3.11 | 3.26 | 0.20 | + 0.07 |
| Ca | $\bar{x}$ | 18.0 | 0.65 | 25.4 | 31.2 | 3.63 | 13.6 | 0.10 | | |
| | solution 1000 gm/l | 18.34 | - | 25.74 | 31.22 | 3.50 | 13.7 | - | 0.20 | - 0.21 |
| | 100 mg/l | 17.7 | 0.15 | 25.30 | 31.05 | 3.25 | 13.35 | 0.10 | 0.20 | + 0.15 |
| Mg | $\bar{x}$ | 1.99 | 0.66 | 0.60 | 0.62 | 0.33 | 2.80 | 1.96 | | |
| | solution 1000 mg/l | 1.99 | 0.60 | 0.35 | 0.58 | 0.30 | 2.72 | 1.78 | 0.11 | + 0.04 |
| | 100 mg/l | 1.94 | 0.55 | 0.30 | | | 2.65 | 1.75 | 0.17 | + 0.10 |
| Ti | $\bar{x}$ | 0.106 | 0.043 | 0.37 | 0.32 | 0.047 | 0.12 | 0.015 | | |
| | solution 1000 mg/l | 0.107 | 0.046 | 0.35 | 0.32 | 0.051 | 0.14 | 0.016 | 0.011 | - 0.001 |
| | 100 mg/l | 0.101 | 0.039 | 0.35 | 0.31 | 0.046 | 0.14 | 0.015 | 0.013 | + 0.003 |
| Mn | $\bar{x}$ | 0.69 | 0.13 | 5.80 | 1.32 | 1.31 | 1.10 | 1.06 | | |
| | solution 1000 mg/l | 0.69 | 0.125 | 5.69 | 1.36 | 1.37 | 1.02 | 1.01 | 0.066 | + 0.01 |
| | 100 mg/l | 0.69 | 0.15 | 5.70 | 1.21 | 1.16 | 0.83 | 1.59 | 0.21 | + 0.17 |
| P | $\bar{x}$ | 0.35 | 0.010 | - | 3.69 | 0.128 | 0.80 | - | | |
| | solution 1000 mg/l | 0.36 | - | - | 3.73 | 0.103 | 0.77 | - | 0.033 | 0 |
| | 100 mg/l | 0.33 | - | - | 3.56 | 0.122 | 0.69 | - | 0.23 | + 0.18 |

zation of the X-ray fluorescence [3]. The analysis of the seven ironwork products with the assistance of this new standardization has led to the results appearing in table 8. For the two dilutions of /408 iron, as well as for the 1000 mg/l solutions of silicon and calcium, the intensities-concentrations regressions have been calculated with the assistance of second degree equations. The examination of this table indicates the disappearance of the systematic deviation previously observed with the standardization by synthetic solutions. It also demonstrates that the use of dilute solutions and the measurement with the internal standard does not improve the quality of the result. The precision obtained with the standardization by "synthetic samples" on the contrary is very acceptable.

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TABLE 8. RESULTS OBTAINED WITH STANDARDIZATION BY "SYNTHETIC SAMPLES".

| | | 679-1 | 680-1 | 878-1 | 879-1 | 876-1 | PHF-2 | 610-1 | σ % | σ % ref.-ICP |
|---|---|---|---|---|---|---|---|---|---|---|
| Fe | $\bar{x}$ | 26.2 | 59.9 | 0.60 | 18.9 | 26.85 | 31.7 | 67.6 | | |
| | solution 1000 mg/l | 24.8 | 59.5 | 0.71 | 19.6 | 26.71 | 31.2 | 67.8 | 0.38 | + 0.03 |
| | 100 mg/l | 23.8 | 60.2 | 1.03 | 18.85 | 26.22 | 30.95 | 67.16 | 0.6 | + 0.19 |
| Si | $\bar{x}$ | 3.6 | 6.2 | 15.7 | 6.12 | 1.71 | 5.66 | 3.16 | | |
| | solution 1000 mg/l | 3.52 | 6.36 | 15.3 | 6.26 | 1.97 | 5.73 | 3.26 | 0.22 | - 0.08 |
| | 100 mg/l | 3.84 | 6.30 | - | 6.22 | 2.59 | 5.81 | 3.01 | 0.35 | - 0.29 |
| Ca | $\bar{x}$ | 18.0 | 0.65 | 25.6 | 31.2 | 3.63 | 13.6 | 0.1 | | |
| | solution 1000 ppm/l | 18.16 | 0.56 | 25.80 | 31.96 | 3.10 | 13.32 | 0.27 | 0.38 | - 0.16 |
| | 100 mg/l | 18.77 | 0.18 | 25.98 | 32.22 | 3.30 | 13.81 | - | 0.66 | - 0.39 |
| Al | $\bar{x}$ | 1.99 | 0.66 | 0.60 | 0.62 | 0.33 | 2.0 | 1.96 | | |
| | solution 1000 mg/l | 2.00 | 0.50 | 0.50 | 0.52 | 0.29 | 2.75 | 1.90 | 0.07 | 0 |
| | 100 mg/l | 2.10 | 0.55 | 0.00 | 0.55 | 0.23 | 2.00 | 1.86 | 0.22 | - 0.07 |
| Ti | $\bar{x}$ | 0.106 | 0.045 | 0.37 | 0.32 | 0.047 | 0.12 | 0.015 | | |
| | solution 1000 mg/l | 0.106 | 0.037 | 0.36 | 0.33 | 0.042 | 0.15 | 0.002 | 0.015 | 0 |
| | 100 mg/l | 0.106 | 0.037 | 0.35 | 0.32 | 0.041 | 0.169 | 0.002 | 0.019 | + 0.002 |
| Mg | $\bar{x}$ | 0.69 | 0.14 | 5.8 | 1.32 | 1.31 | 1.1 | 1.86 | | |
| | solution 1000 mg/l | 0.66 | 0.166 | 5.63 | 1.30 | 1.28 | 0.99 | 1.86 | 0.08 | + 0.047 |
| | 100 mg/l | 0.71 | 0.16 | 5.74 | 1.36 | 1.33 | 1.01 | 1.83 | 0.005 | + 0.001 |
| P | $\bar{x}$ | 0.35 | 0.018 | 0.013 | 3.69 | 0.128 | 0.8 | 0.007 | | |
| | solution 1000 mg/l | 0.533 | 0.004 | 0.000 | 3.56 | 0.103 | 0.758 | - | 0.07 | + 0.03 |
| | 100 mg/l | 0.50 | 0.017 | 0.110 | 3.22 | 0.091 | 0.65 | - | - | |

The oxide samples prepared with the Plasmasol with the assistance of the Fluosid 21 flux, to which there has been added strontium nitrate, can be analyzed by ICP-SEO. The results obtained are precise with the condition of employing either a standardization by MRC or a synthetic standardization constituted from pure compounds.

## Case of Pre-Reduced Iron Minerals

Among the ironwork products called upon to be analyzed, there exist those which contain more or less significant quantities of elements in the reduced state. This is the case for the pre-reduced iron minerals; this is also the case for the steelowrk dusts and for the used fireclays. While the analytical requirements are less crit-

TABLE 9. RESULTS OBTAINED FOR THE PRE-REDUCED IRON MINERAL 658-1. REPRODUCIBILITY TEST AND RESULTS OF ANALYSIS BY ICP-SEO.

| | Fe | Si | Ca | Al | Ti | Mg | P | Mn |
|---|---|---|---|---|---|---|---|---|
| $\bar{x}$ | 91.10 | 0.795 | 0.139 | 0.320 | 0.220 | 0.239 | 0.017 | 0.042 |
| $s_M$ | 0.27 | 0.032 | 0.013 | .0.014 | 0.010 | 0.006 | 0.001 | 0.003 |
| ICP | 90.74 | 0.879 | 0.163 | 0.316 | 0.220 | 0.230 | 0.031 | 0.042 |
| $s_R$ | 0.51 | 0.023 | 0.007 | 0.005 | 0.002 | 0.002 | 0.002 | 0.002 |
| $s_r$ | 0.48 | 0.021 | 0.002 | 0.001 | 0.001 | 0.001 | 0.003 | 0.002 |
| d | - 0.36 | - 0.084 | - 0.026 | + 0.004 | 0 | - 0.011 | - 0.014 | 0 |

$\bar{X}$ certified value of MRC

$s_M$ standard deviation of the certificate

ICP mean value for the ICP-SEO analysis

$s_R$ standard deviation for ten preparations

$s_r$ standard deviation for ten measurements

d difference between the certified value and ICP value

ical for these last two, it is not the same for the pre-reduced minerals. The use of the Plasmasol in order to place into solution these particular samples can present a certain advantage in the measurement or a gain of time can be realized with respect to the other methods of attack or dissolution.

For this type of product, it is indispensable to pass through a pre-oxidation stage before proceeding with the fusion-dissolution.

In their works concerning the use of the PERL'X for the preparation of the ferro-alloys, Petin and Wagner [4] stipulated a composition of flux of an almost general effectiveness. Without going up to /409 such a complete flux, the IRSID was inspired by these works to select a mixture which could effectively place into solution the pre-reduced iron minerals. The oxidants proposed by Petin and Wagner include sodium carbonate, sodium nitrate, potassium nitrate and strontium nitrate. Thus, between 380 and 850°C, the sample is always surrounded by an oxidant in liquid form capable of transforming the metallic particles into oxides. In the case of the utilization of the composite crucible, this mixture can not be employed following adherence of

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the vitreous carbon. The selection of the flux is thus centered on Fluosid and strontium nitrate with the respective proportions of 2 and 1. The diagram for the preparation is indicated in figure 7. The first phase of the preparation, this the oxidation phase, is carried out at 850°C with stirring and it lasts 4 minutes. The final phase of the fusion occurs at 1050°C and lasts 3 minutes.

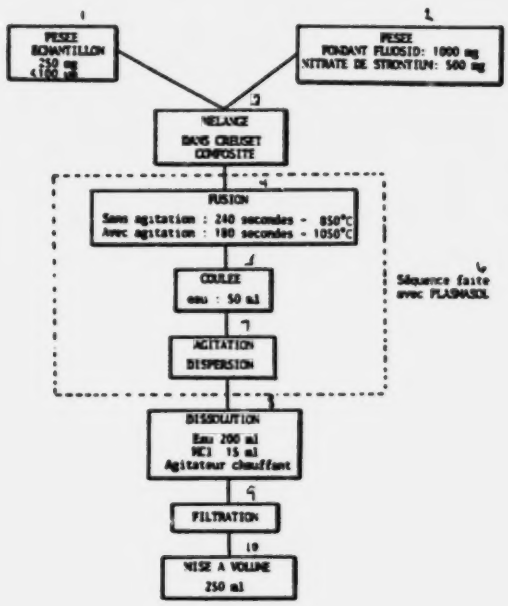


Figure 7. Diagram of the preparation of the pre-reduced minerals.
Key: 1-Sample weight 2-Weight, Fluosid flux: 1000 mg, strontium nitrate: 500 mg 3-Mixture in composite cricible 4-Fusion, without stirring: 240 seconds-850°C, with stirring: 180 seconds-1050°C 5-Pouring, water: 50 ml 6-Sequence made with Plasmasol 7-Stirring, dispersion 8-Dissolution, Water 200 ml, HCl 15 ml, Heating stirrer 9-Filtration 10-Return to volume.

The tests for preparation and analysis have been carried out on a single sample-type, MRC 685-1. Synthetic solutions have served for the standardization.

The results obtained are indicated in table 9. There appears

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TABLE 10. RESULTS OBTAINED WITH VARIOUS METHODS OF ANALYSIS. MRC 685-1.

| | | | ICP-OES | AAS | VOLUMETRY |
|---|---|---|---|---|---|
| Fe | $\bar{x}$ | 91.1 | | | |
| | s | 0.27 | | | |
| | anal. result | | 90.76 | | 91.38 |
| | $s_R$ | | 0.31 | | 0.19 |
| Si | $\bar{x}$ | 0.793 | | | |
| | s | 0.032 | | | |
| | anal. result | | 0.87 | | |
| | $s_R$ | | 0.04 | | |
| Al | $\bar{x}$ | 0.320 | | | |
| | s | 0.014 | | | |
| | anal. result | | 0.326 | 0.297 | |
| | $s_R$ | | 0.008 | 0.007 | |

$\bar{X}$ : certified value

s : standard deviation of the certificate

$s_R$ : standard deviation for ten preparations

AAS :atomic absorption spectrometry

volumetry: volumetric method of titration of the iron recommended by the ISO

in this table:

-the composition of the MRC

-the interlaboratory standard deviation of the certificate of analysis

-the mean of the ICP-SEO results

-the reproducibility of 10 preparations

-the reproducibility of 10 measurements

-the certified value-ICP value difference.

The measurements of the iron have been run by making use of a second degree standardization. It is necessary to remark on the significance of the dispersion of the measurements in the case of the iron. It is 0.48%, while the preparation dispersion and measurement dispersion is 0.51%. This imprecision, significant in absolute value, however is low in relative value (0.45%). It would be desirable to have more stable when analyses of this type are carried out. These results do not call for practically any other comments, except perhaps the observation of a very slight tendency to over titrate, this

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capable of being due to the quality of the reactants having served to prepare the synthetic solutions for standardization.

These same preparations of the MRC 685-1 have been employed for the titration of aluminum by atomic absorption spectrometry and that of iron by volumetry. The results are indicated in table 10. The quality of the results prooves that the preparations made by the Plasmasol lead to solutions capable of being analyzed by other techniques of titration.

## Conclusions

The preparation of the samples is a fundamental task in an analysis laboratory. It is often long and difficult and it necessitates experienced and competent personnel. In the face of modern and rapid analytical methods, it is necessary to design and realize automations capable of preparing the samples. Attempts have been made in this direction and several devices exist on the market. The Claisse-Fluxer [5] employs gas as the energy source and it is, due to this fact, noisy and polluting. The Labrob [6] is well adapted for the preparations necessitating an enrichment phase in view of the titration of traces. The Atom 30 [7] allows the continuous preparation of great series of samples, but there is need for a significant number of platinum cricibles and its use if very costly. The apparatus designed by the IRSID and called Plasmasol allows the placement into solution of the oxide products and partially metallic ones in a short time, without noise and without pollution, while only making use of a small quantity of platinum.

The solutions obtained are capable of being analyzed by ICP-SEO, possibly by other chemical or physico-chemical methods and lead to the same results as the manual methods of preparation by placement in acid solution or by fusion in the muffle furnace [8, 9]. However, the results obtained by ICP-SEO are characterized by a relatively high dispersion of the measurement with respect to that due to the preparation by the Plasmasol. In other respects, a great carefulness

must be standard when attempts are made in order to proceed with the standardization of the ICP-SEO by synthetic solution. In fact it appeared that systematic deviations can be observed by starting with such solutions. It is thus highly recommended to standardize either with the assistance of certified reference materials, or with synthetic samples prepared with pure compounds and simulating the matrix.

Experimented up to now only in the ironworks range, it is practically certain that the Plasmasol can find uses in the other sectors of the industry and in research. However, it must be recalled that for each new type of product to be placed into solution, it is indispensable to determine the appropriate flux and to find the right operatory parameters. With this in mind, the placements into solution are also as good, or even better, than the manual ones.

## REFERENCES


1. IRSID Patent, AFBI 667 (07-24-80), Inventors: G. Willay and A. Wittmann.

2. IRSID Patent, AFBI 661 (06-12-80), Inventor: G. Willay.

3. Staats, G., personal communication.

4. Petin, J and A. Wagner. Laborpraxis 7/5, 416-419 (1983).

5. Brenner, I.B., I. Gal, H. Eldad, L. Halicz and D. Dorffer, ICP Information Newsletter 8/10 (1983).

6. Govindaraju, K., 23rd International Spectroscopicum Colloquim.

7. Borsier, M. and M. Garcia, International Conference on Industrial Inorganic Element Analysis, 1981, Proceedings: N.L. Phillips (Ed.).

8. Hancart, J., International Conference of Industrial Inorganic Element Analysis, 1981, Proceedings: N.L. Phillips (Ed.).

9. Ohls, K., Developments in atomic plasma spectrochemical analysis, R.M. Barnes (Ed.), Heyden.